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EVALUATION OF OIL SHALE FROM EASTERN CANADA BY RETORTING AND BY CONCENTRATION OF A KEROGEN-RICH FRACTION

Final Report by

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SUMMARY

An apparatus was developed for testing the retorting behaviour of oil shales under pressures up to 500 psi hydrogen and 700°C. Equipment was also constructed and brought into service for the determination of oil yields by the Fischer assay method.

Six samples of Albert Shale of varying oil content (<10 to 40-50 gals/ton) were tested by the Fischer method and by hydrogen retorting to determine yields of liquid distillate under different conditions of retorting. The Fischer assays gave oil yields of 2.9 to 47.5 gals/ton which corresponded to carbon conversion of 50.5 to 87.8 per cent. This rate of conversion was higher than expected because eastern US Devonian Shales show low conversion rates of 25 per cent. The higher conversion rate is probably related to the fact that the New Brunswick shales are younger, of Carboniferous age, and probably contain more hydrogen than their older US counterparts.

The hydrogen retorting tests at 700°C and 500°C gave carbon conversion rates of 53 to 87 per cent which are comparable to that for the Fischer retorting. Retorting at 500°C gave oil yields similar to the Fischer assay but at 700°C oil yields were reduced, 4 to 30 gals/ton, although gas yields increased. Hence, in the retorting tests performed, the use of hydrogen at 500 psi did not increase yields.

More work is needed to understand the retorting behaviour of New Brunswick and other Canadian oil shales. Retorting tests for resource assessment purposes are also needed. These should be coupled to determining the rate of carbon conversion and hence the effectiveness of the retorting technique.

Petrographic, chemical and thermogravimetric analyses of the oil shales was undertaken to characterize the materials for retorting tests. The so-called shale is a laminated kerogenous dolomitic marlstone. On heating devolatilization starts before 300^{o}C and is essentially complete by 700^{o}C when decomposition of the carbonate commences.

The second part of the project involved producing a kerogen concentrate by standard beneficiation methods viz size separation, spherical agglomeration, gravity methods and by flotation. Only gravity separation showed promise of being a viable industrial process. Fine grinding and gravity separation gave high concentrations up to 70 gals/ton but yields were low.

EVALUATION OF OIL SHALE FROM EASTERN CANADA BY RETORTING AND BY CONCENTRATION OF A KEROGEN-RICH FRACTION

CANMET CONTRACT

There were two parts to the present work with the Energy Research Program Office of CANMET under the contract "To evaluate oil shales from eastern Canada and to investigate concentrating kerogen rich oil shale components" (Appendix 1)

Retorting

The main task of the project was to design, build and bring into operation an apparatus to retort the oil shale under hydrogen pressures. At the same time a competence to perform conventional thermal retorting tests by the Fischer method would be established.

A series of six samples of New Brunswick oil shale of differing oil content would be analyzed for extractable oil by the Fischer method and by hydroretorting in the apparatus designed for that purpose (Appendix 2). A comparison of the results would establish the advantages of retorting under hydrogen pressures. All work would be accompanied by the appropriate analysis.

Concentration of Kerogen Components

As much of the New Brunswick oil shales are low grade beneficiation to produce a kerogen enriched fraction for subsequent use could be attractive. Shale was to be treated by standard methods of upgrading to test the degree to which the kerogen could be separated and concentrated.

BACKGROUND

Hydrogen Retorting

This work was undertaken on the basis that the distillation behaviour of the oil shales of New Brunswick were similar to those of Devonian age in the eastern US for which a technology for extracting a petroleum product has been proposed (Feldkirchner et al 1979). Eastern oil shales in North America, which includes the Carboniferous shales of eastern Canada, are generally low grade containing less than 10 gals/ton oil compared to the western occurrences in Wyoming, Colorado and Utah which contain at least 20 gals/ton. The oil is contained in the solidified hydrocarbon, kerogen, which in western oil shales has a carbon hydrogen ratio of 7:8. Eastern US oil shales are said to be deficient in hydrogen with the result that when heated for the Fischer assay or conventional retorting process the hydrogen-poor kerogen is converted to coke. By contrast, most of the hydrogen-rich kerogen of western oil shale is converted to oil. Some 70 to 80 per cent of carbon remains in eastern US oil shales after the conventional Fischer retorting test. Thus, the Fischer analysis, that used in the past to assess eastern oil shales, could minimize the possible hydrocarbon recovery because so much remains as coke.

According to the Institute of Gas Technology (IGT), Chicago, the full potential of eastern low grade oil shales in terms of energy recovery could possibly be attained by retorting under hydrogen pressure. Coking would be reduced and yields of medium boiling point components would be increased. Hydro-retorting tests at the Institute of Gas Technology, Chicago, on Kentucky oil shale, the eastern type, with a Fischer assay of 10 gal/ton gave a product yield of 25 gal/ton oil and 2000 SCF/ton SNG. Ninety per cent of the carbon was recovered compared to about 35 per cent by conventional retorting. Application of high hydrogen partial pressure at low heating rates increases recovery 2½ times over that obtained by conventional combustion retorting (Figure 1).

Hydro-retorting would be an expensive way of processing, but there could be benefits which would justify the extra cost. About 70 per cent of the oil is in the middle distillate range, which requires less subsequent refining than heavier crudes. Desulphurization and removal of nitrogen would still be necessary in the course of producing saleable products. Hydro-retorting, in addition to higher yields, is a flexible process because production can be easily changed from predominantly oil to gas output (SNG)(Table 1). The search for additional supplies of motor fuels makes the oil shales increasingly attractive as an alternative source.

Recently, it was announced that Bechtel will study the commerical flexibility of Phillips Petroleum's advanced retorting process for shale oil. Work will be in the eastern Devonian oil shales by IGT's "Hytort" process which is based on retorting under hydrogen pressures (Chemical Week, October 14, 1981).

The early attempts at hydrogen treatment were by the Pyrochem method (Oil and Gas Journal, March 1964). The IGT technology appears to be based on this process where hydrogen apparently plays a triple role of chemical reactant, heat transfer agent and partial pressure reducer. This uncatalysed destructive distillation in hydrogen of the oil shale did result in increased oil recovery. Yields were raised to 115 per cent in the Pyrochem process of Huntington (1966) and, as mentioned previously, by 2-3 times in the IGT Hytort process. There do not appear to be an "tricks" with either process. Both have controlled heating of oil shale in a hydrogen atmosphere but the Hytort process does have a double reactor system (Weil and others 1978).

Other Activities

Oil shales of New Brunswick are the best known and are receiving the most attention of any in Canada. Canadian Occidental Corporation Ltd. and Petro Canada have leased concessions and others are under negotiation with mining

companies. The Mineral Resources Branch of the New Brunswick Department of Natural Resources has an active program of resource evaluation which is linked to that of the Institute of Sedimentary and Petroleum Geology (GSC) Calgary, and is funding a research program at the Research and Productivity Council, Fredericton on the fluidized bed combustion of oil shale mixed with coal.

TABLE 1

HYDROCARBON RECOVERY FROM EASTERN OIL SHALES (U.S.A.)

		Hydroretroting	
	Combustion Retorting	High liquid Yield	High gas Yield
Oil gal/ton	10	25	9
Gas SCF/ton	450	1800	5100
Carbon Recovery	32	84	81

Information from I.G.T., Chicago

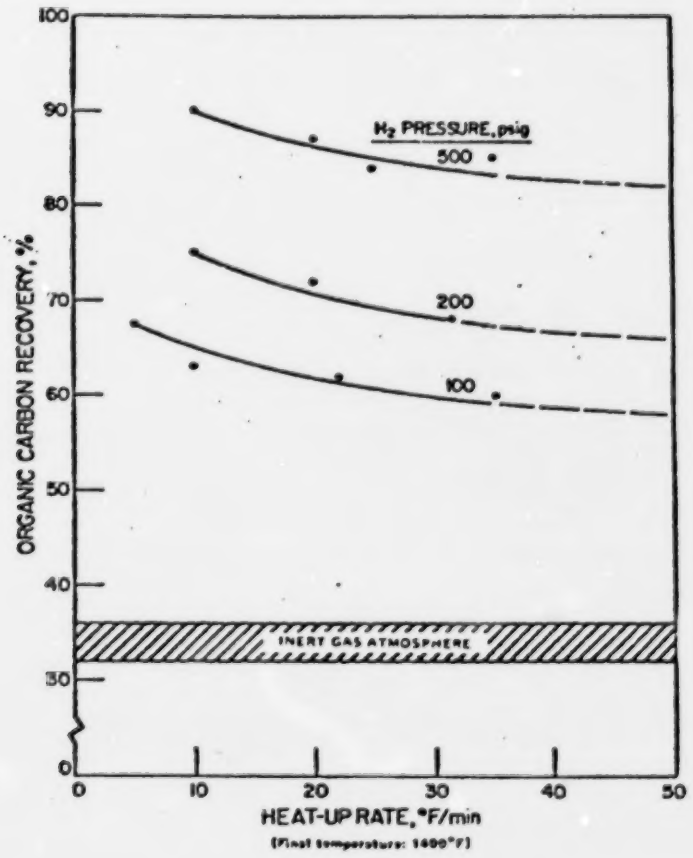


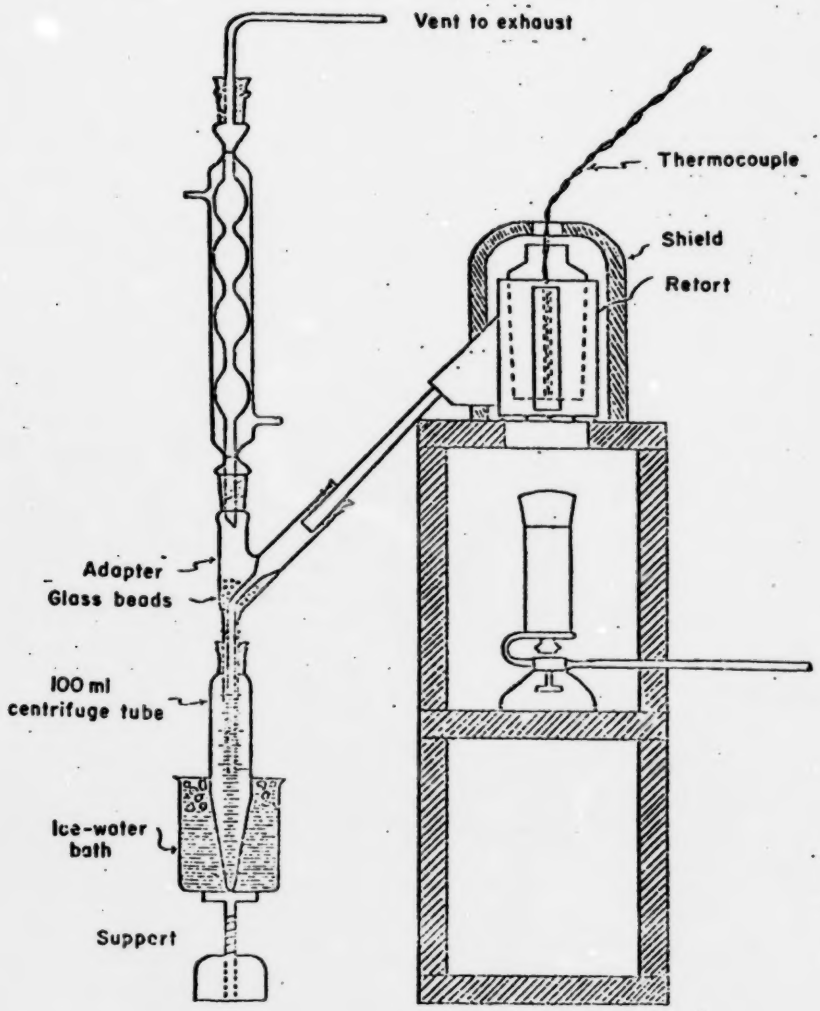
Figure 1 — ORGANIC CARBON RECOVERY WITH EASTERN SHALE IN HYDROGEN

PROCESS DEVELOPMENT ONE

Fischer Retorting

The Fischer assay was developed for determining potential oil yield because this method has been the traditional one and that used widely by industry. The US Bureau of Mines analyses consists of heating a 100 gram sample of -8 mesh oil shale to 500^{o}C in 40 minutes and maintaining this temperature for another 40 minutes. The distillate is collected and the amount of evolved oil, water and, by weight loss, gas calculated (Stanfield and Frost 1946). The method is precise and reproducible under well controlled conditions and the results, in terms of gallons of oil per ton shale, are useful for resource evaluation but not for processes. Process yields are invariably higher than for the Fischer assay. Thermal chromatography, in which evolved gasses are monitored are likely to be more widely used to measure oil contents in the future (Miknis F. P. 1979).

Retorts were made at RPC according to the specifications of the US Bureau of Mines apparatus (Figure 2). The results of Fischer assays on the 5 drill core samples and the surface outcrop material are given in Table 2. The proximate analysis of the spent shale together with the major and minor element composition follows in Table 3 and trace elements in Table 4. See appendixes 7 and 8 for additional compositional data.



FISCHER RETORT APPARATUS
FIGURE 2

TABLE 2

FISCHER ASSAY OF OIL SHALE

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Fischer Assay wt%						
Oil	1.24	2.69	3.34	7.97	11.28	20.30
Water	4.75	2.95	2.33	1.26	0.98	0.91
Gas loss	3.01	1.36	3.08	1.77	3.28	3.79
Oil Characteristics						
Gals/ton	2.9	5.1	10.1	18.6	26.6	47.5
SG $60^{o}F/60^{o}F$	0.870	0.873	0.857	0.866	0.871	0.880
Btu/lb	18825	17690	19188	17763	18558	18860
Sulphur	0.46	0.27	0.66	0.92	1.09	1.03
Calorific Value BTu/lb						
Spent shale	26	408	123	185	640	935
Number of Determination in average	4	4	2	4	3	2

Imperial gals/short ton

TABLE 3

COMPOSITION OF SPENT SHALE FROM FISCHER ASSAY

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Ash	97.23	90.59	91.71	80.16	82.94	81.63
Volatiles 950°C	5.09	10.38	11.31	17.16	18.94	19.00
Sulphur	0.80	0.07	0.70	0.72	0.94	0.51
Mineral Carbon	0.80	0.40	0.20	2.70	2.70	5.00
Organic Carbon	0.20	2.40	2.00	2.40	3.20	2.80
Major and Minor Elements wt%						
SiO_2	54.76	53.84	51.22	43.76	42.71	44.82
Al_2O_2	16.50	24.74	18.76	24.51	21.88	28.04
Fe_2O_3	8.76	8.79	6.65	5.32	4.72	4.62
MgO	3.20	1.24	3.10	3.76	2.74	2.96
CaO	0.16	1.00	0.64	10.31	13.08	10.56
Na_2O	1.09	1.05	1.27	1.12	1.21	1.21
K_2O	1.46	1.78	1.32	0.92	0.77	0.78
P_2O_5	0.34	0.34	0.17	0.34	0.69	0.57
MnO	0.08	0.18	0.08	0.09	0.10	0.09
TiO_2	0.42	0.42	0.63	0.42	0.42	0.42

TABLE 4

TRACE ELEMENT COMPOSITION OF SPENT SHALE FROM FISHCER ASSAY

Trace Elements (ppm)	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Antimony	-	-	-	-	-	-
Arsenic	-	-	-	-	-	-
Barium	500	1000	1000	1000	1000	1000
Beryllium	2	2	2	1	1	1
Bismuth	-	-	-	-	-	-
Boron	200	100	200	100	100	100
Cadmium	-	-	-	-	-	-
Cerium	-	-	-	-	-	-
Chromium	100	50	100	50	30	30
Cobalt	10	10	10	10	-	-
Copper	5	50	5	5	30	30
Gallium	20	20	20	10	10	10
Germanium	-	-	-	-	-	-
Lead	50	20	50	20	20	20
Lithium	-	-	-	-	-	-
Molybdinum	-	10	10	10	10	10
Nickel	50	30	50	50	20	20
Phosphorus	-	-	-	-	-	-
Silver	< 3	< 3	< 3	< 3	< 3	< 3
Strontium	500	500	500	1000	1000	1000
Thorium	-	-	-	-	-	-
Uranium	-	-	-	-	-	-
Vanadium	100	100	100	100	100	100

- Sought but not found

PROCESS DEVELOPMENT TWO

Hydrogen Retorting

The apparatus first constructed, based on that of Huntington (1966) was designed to pass hot hydrogen over pulverized oil shale and to collect, initially, the condensed distillate at pressure. Further collection of liquid and gas distillate would be at room pressures. The pipe reactor of 304 stainless steel tubing consisted of a lower preheat section filled with steel balls, a central portion for the sample and a top part which could be used for a catalyst. The sample was retained in the central section by metal gauze and an inert fiber. The pipe reactor was electrically heated with samox tape which was covered with insulation during runs. The condensate was collected at pressure in a kuentzel type pressure vessel (Plate 1). Design details were discussed with ERL staff in December 1981 and their approval obtained before construction commenced. The schematic for the pyrochem reactor is shown in Figure 3 and details of the engineering drawings are given in Appendix 3 A-E. Difficulties which necessitated major equipment re-design were:

1. Cone-fit hydraulic mode couplings on the reactor tube leaked and were replaced by copper gasketed flange-fit vacuum couplings.

2. Preheat section "blew out" through localised overheating. Additional thermocouples had to be added for better temperature control.

3. The large condenser and kuentzel bomb collector were unsuited for the small amount of liquid distillate to be trapped and were replaced by a Fischer type collection system.

The apparatus which finally functioned satisfactorily retained the flange couplings or the reactor pipe, but the preheat section was shortened to 18 inches and temperature monitored. The catalyst section was removed and a direct "crack" value leading to a normal Fischer assay condensing and collecting system substituted for the pressurized unit (Figure 4, Appendix 4a,b).

The original Pyrochem work described the use of a catalyst. A cobalt molybdenum catalyst was claimed to be immune to poisoning by nitrogen or sulphur. A catalyst was not employed in the present work because the problems of catalyst poisoning were considered to be real and because the major purpose of this first study was to obtain information on yields using only distillation under hydrogen pressure. Other factors would have to be determined in subsequent work which would lead to a thorough understanding of the physico-chemical parameters of distillation and hence the optimization of the retorting process. With the modified equipment process conditions were optimized to maximize yield by:

i show heating rate 4.6°C/min. over 2½ hours.

ii retorting to a maximum temperature of 700°C.

iii using hydrogen pressure of 500 psi.

These experimental conditions were adopted from the IGT work which had shown that yields were best at 500 psi hydrogen and at slow heating rates. In addition, Arnold (1975) had demonstrated the advantages of low heating rates in pyrolysis experiments which showed that increasing the heating rate from 4°C/min. to 40°C/min. decreased the yield of oil and gaseous organic product by 23 per cent.

Retorting at 700°C

Single lots of six oil shales, previously analyzed by Fischer assay, were hydrogen retorted. Conditions in each case were:

a) Sample size - variable because of different bulk densities. Range from ∿90g for 'A' to ∿60g for 'E'.

b) 500 psi of hydrogen + 1% helium during retorting at 750 ml/min.

c) Total time from ∿17°C to 700°C for sample (reactor) section = 2½ hours.

No attempt was made to analyze 'effluent' gases. However, the bulk of the material condensing in the liquid N_2 trap was water suggesting significant amounts of water after the ice-water cooled condenser. Results are calculated on a single measured specific gravity of oil (Sample E) of 0.790 (Table 5). The proximate analyses of the spent shale are in Table 6.

Retorting at 500°C

During a review meeting with Dr. H. Sawatzky, it was agreed that we should do further tests under conditions nearer to those of Fischer retorting. In particular, we should retort at 500°C and consider replacing alumina fibre used to hold the "charge" in the reactor unit with other more catalytically inert fibre.

The six samples of oil shale were retorted using asbestos fibre to hold the "charge". Conditions in each case were:

a) Sample size - variable from ∿90g for sample A to ∿60g sample E.

b) Warm up time from 15°C to 500°C, 1 hour with subsequent hold time of 40 minutes.

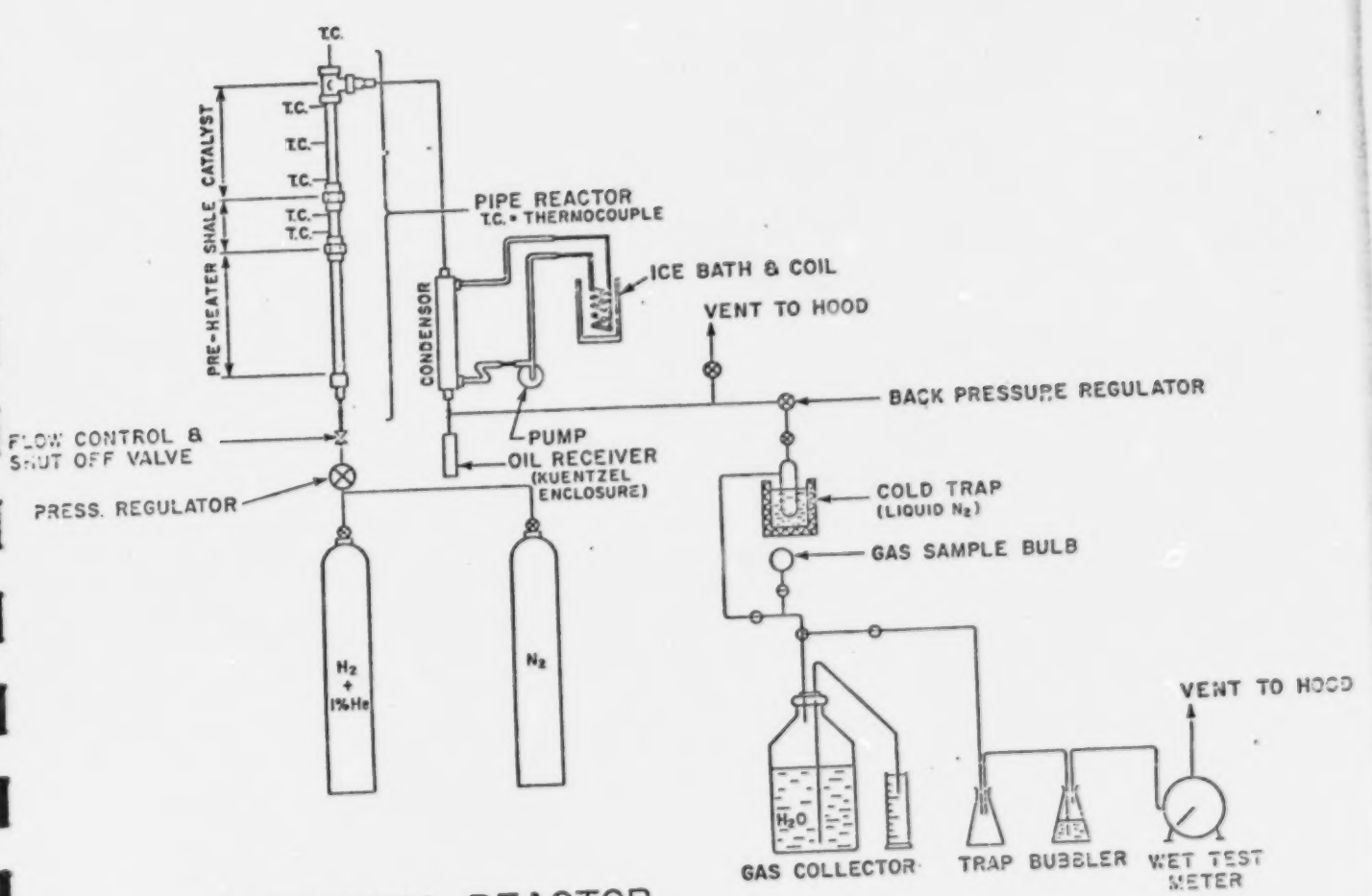
c) 500 psi hydrogen + 1% helium at 750 ml/min.

In most cases the effluent gases were analyzed with a G.C. analyzer. Invariable the effluent gas consisted of carrier gas plus, qualitatively, small amounts of carbon dioxide, methane, >ethane, and >propane. The solid condensed in the liquid nitrogen trap consisted of approximately equal amounts of volatile gas - principally methane and ethane and of aqueous sulphurous liquid together with small amount of volatile light oil.

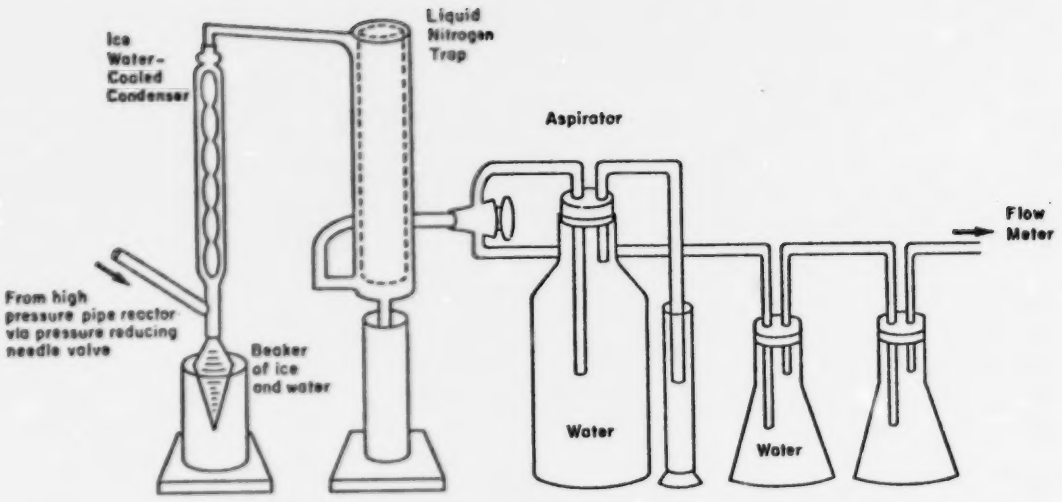
Results of hydrogen retorting at 500°C are given in Table 5 and the composition of the spent shale in Table 6.

Analysis of Oils

Three composite samples of oil from the Fischer tests and hydrogen retorting at 700°C and 500°C were analyzed (Table 7). These three samples were also analyzed by temperature programmed gas chromatography. Experimental details are given in Appendix 5. The results shown in Figures 5, 6 and 7 indicate that all three oil samples have similar distillation characteristics and that no significant changes have occurred through hydrogen retorting as compared to the Fischer retorting.



PYROCHEM REACTOR
(SCHEMATIC)
FIGURE 3



EQUIPMENT MODIFICATIONS FOR COLLECTING
DISTILLATE AT ATMOSPHERIC PRESSURE

FIGURE 4

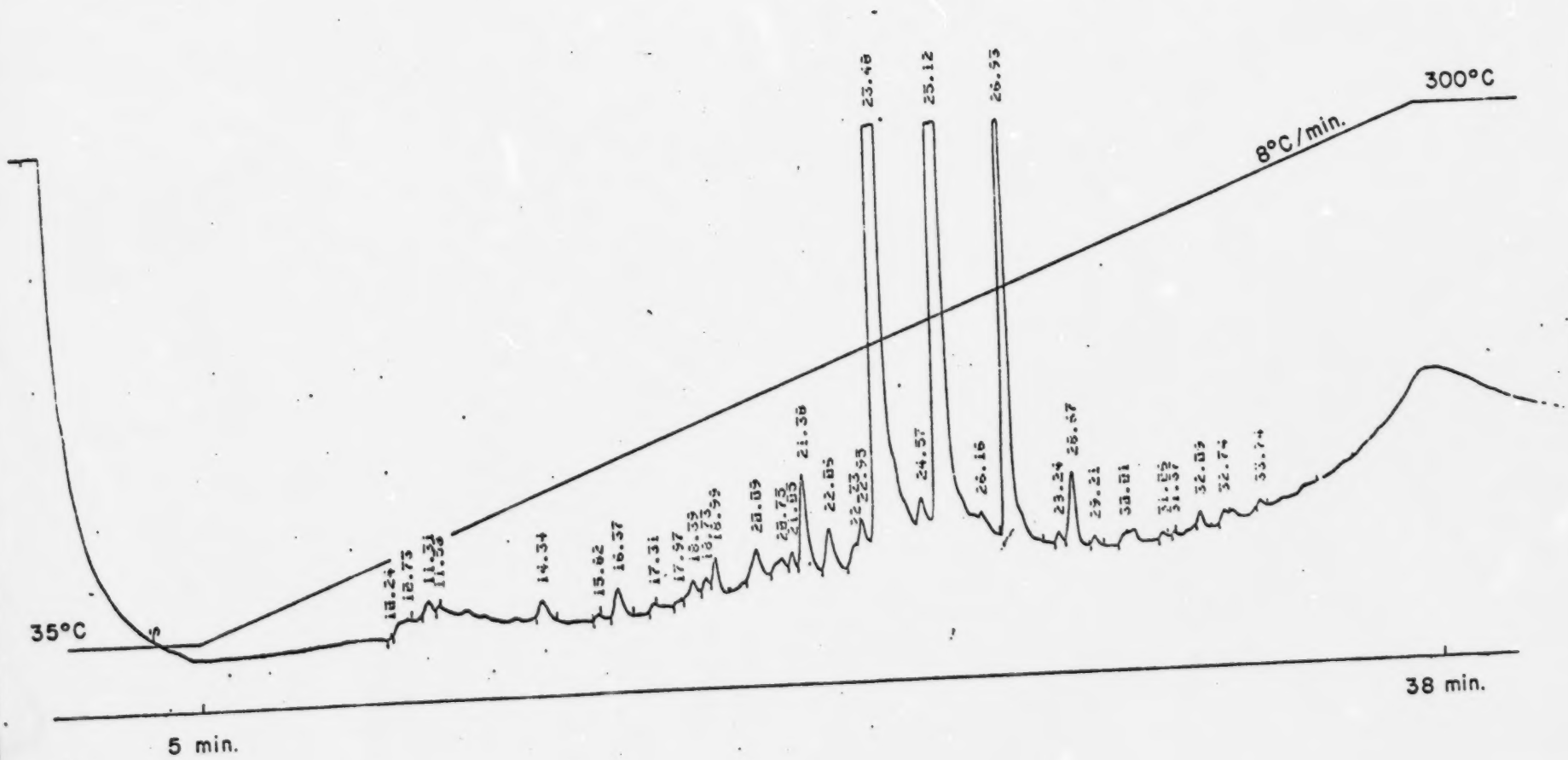


FIGURE 5
G C OF FISCHER OIL COMPOSITE

See appendix 5

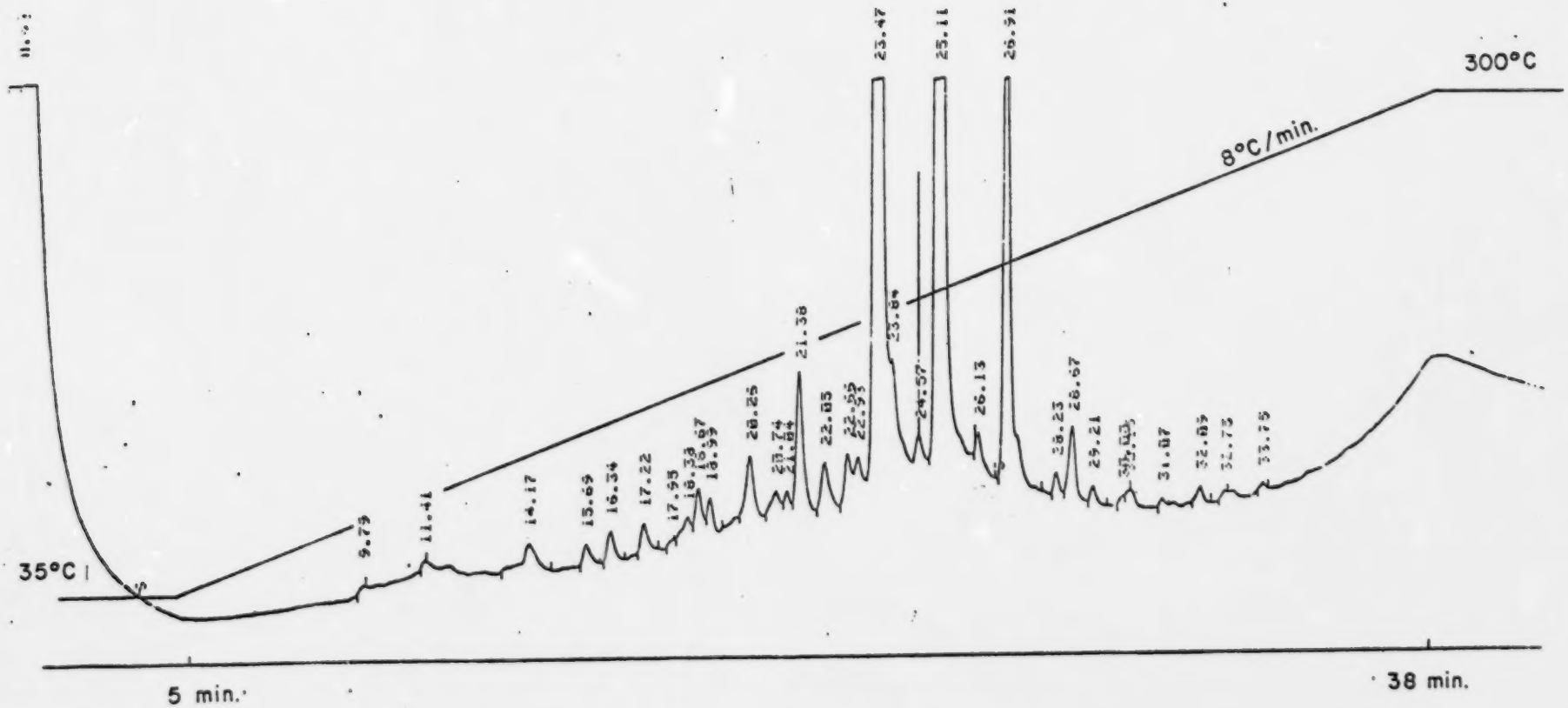


FIGURE 6
G C OF HYDROGEN RETORTING COMPOSITE 700°C

See appendix 5

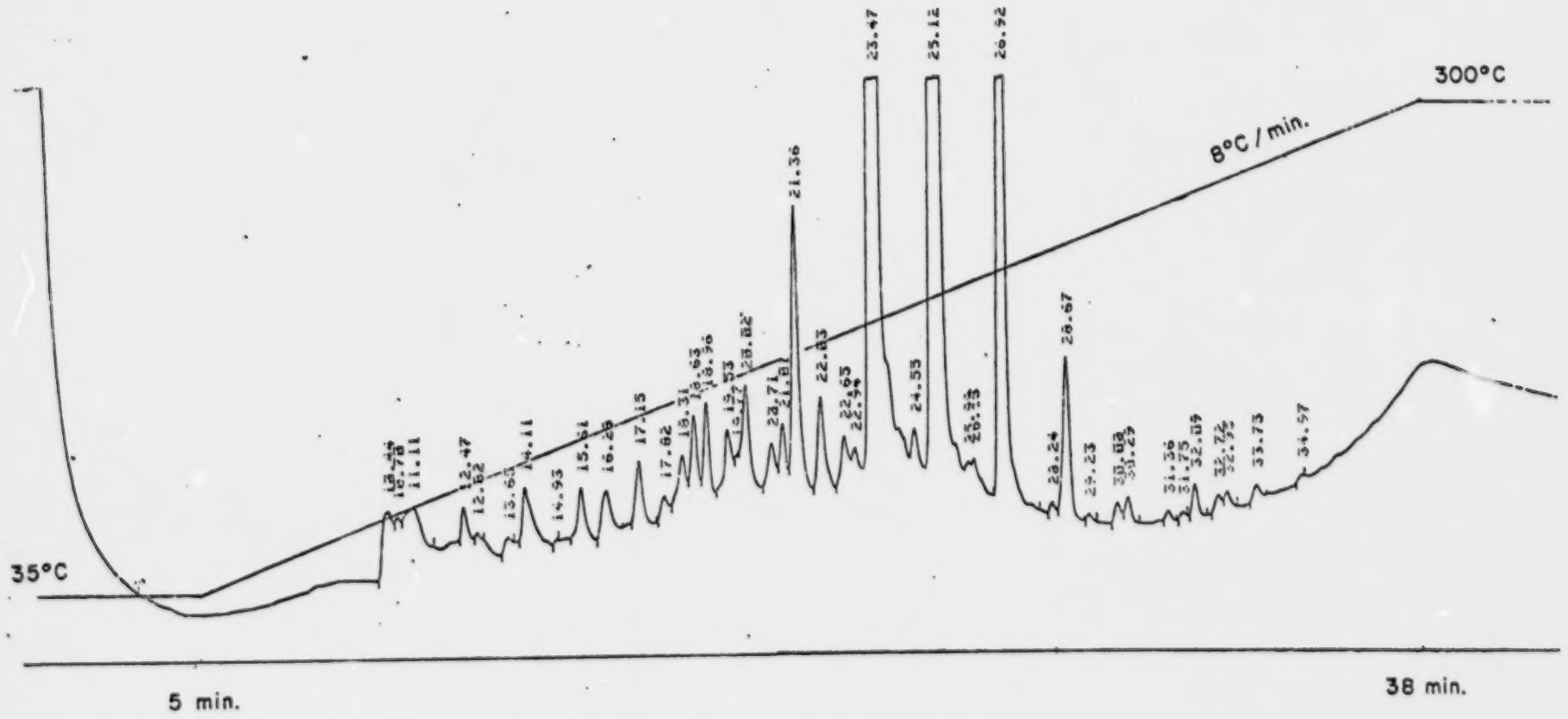


FIGURE 7
G C OF HYDROGEN RETORTING COMPOSITE 500°C

See appendix 5

TABLE 5

RESULTS OF RETORTING UNDER HYDROGEN PRESSURE

Imperial gals/short ton

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
700°C %w/w shale						
Oil	1.95	1.17	2.18	4.53	5.87	12.33
Water	7.30	5.90	2.90	2.00	2.50	3.20
Gas loss	5.35	6.42	10.55	16.13	18.13	20.50
gals/ton	4.3	3.0	5.3	11.5	14.9	31.2
500°C %w/w shale						
Oil	1.82	3.70	3.20	3.88	13.00	19.50
Water	4.70	3.30	7.40	2.10	5.20	1.50
Gas loss	5.70	5.60	4.27	7.96	6.07	5.20
gals/ton	4.2	8.5	7.4	7.8	30.1	45.4

TABLE 6

COMPOSITION OF SPENT SHALE FROM HYDROGEN RETORTING

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Retorting 700°C						
Ash	97.66	98.22	99.52	93.99	95.76	93.36
Volatiles	2.48	3.03	2.04	6.12	5.60	7.00
Sulphur	0.80	0.06	0.94	0.65	1.09	0.66
Mineral Carbon	-	0.08	0.27	0.96	1.28	0.76
Organic Carbon	1.00	1.70	1.04	1.14	1.62	3.66
Btu/lb	148	450	173	256	623	767
Retorting 500°C						
Ash	98.3	94.2	95.5	85.4	92.5	94.3
Volatiles	4.0	5.0	3.2	13.9	7.5	7.4
Sulphur	0.67	0.03	1.07	0.64	0.86	0.64
Mineral Carbon	< 0.1	0.50	0.20	2.94	1.40	1.04
Organic Carbon	0.6	0.99	2.15	2.28	2.4	3.65
Btu/lb	116		378	432	2719	3028

TABLE 7

ANALYSIS OF COMPOSITE DISTILLATE OILS

	Fischer Retorting 500°C	Hydrogen Retorting 500°C	Hydrogen Retorting 700°C
Ultimate Analysis			
Carbon	86.62	85.49	87.14
Hydrogen	12.69	12.23	11.97
Oxygen	0.7	2.2	0.9
Nitrogen	< 0.2	< 0.2	< 0.2
Sulphur	< 0.2	< 0.2	< 0.2
Btu/lb	18481	18117	
SG of oil	0.869	0.790	

Insulated retort pipe with thermocouple temperature recorders on left with principal ice-cooled distillate collector left of centre.

Liquid nitrogen trap in condensate collection system

PLATE ONE

MODIFIED HYDROGEN RETORTING APPARATUS

Insulated retort pipe with thermocouple temperature recorders on left with principal ice-cooled distillate collector left of centre.

Liquid nitrogen trap in condensate collection system

PLATE ONE

MODIFIED HYDROGEN RETORTING APPARATUS

DISCUSSION OF RETORTING TESTS

Results

The results of the retorting experiments can best be assessed by comparing the composition of the raw and spent shale with oil yields and the percentage carbon converted during retorting (Table 8)

The Fischer assays which give, in the six samples tested, oil yields of 2.9 to 47.5 gals/ton corresponding to carbon conversion of 50.5 to 87.8 per cent. (The 90.7 per cent conversion obtained for Sample A could be anomalous). The corresponding hydrogen retorting tests at 700^{o}C gave comparable carbon conversions of 53.0 to 87.6 per cent but with lower oil yields of 4.3 to 37.2 gals/ton. Hydrogen retorting at 500^{o}C again gave similar carbon utilization of 58.7 to 87.4 per cent with oil yields 4.2 to 45.4 gals/ton.

Thus, in each case, carbon conversion to distillate was similar and higher than expected from the IGT work on Devonian shales of the eastern US where carbon conversion rates of 25 per cent were obtained (Figure 1, Table 1).

Matching the similar pattern in carbon conversion is that of yield of distillate. The yield of oil in gals/ton for Fischer assays are similar to that for retorting under hydrogen at 500^{o}C, but gas yields are higher. They are 1.4 to 4.5, averaging 2.5, times that for the Fischer assays.

Hydrogen retorting at 700°C gave lower yields than for both other tests but gas yields were 1.8 to 9.1, average 5.0, times that for the Fischer. The lower oil but higher gas yields might have resulted from cracking part of the oil at 700°C. Conclusions on gas yield must be drawn with care because at the temperatures obtained some dissociation of carbonate to release carbon dioxide could have taken place.

The results for this study are shown graphically in Figure 8 where organic carbon and Fischer assay yields are compared for the New Brunswick Albert shales of Carboniferous age, and the US oil shales of Devonian age. The graph shows the good correlation between organic carbon content and oil yield for the Albert oil shales. It also shows the higher oil yields compared to the US Devonian shales that can be expected from New Brunswick shales of similar carbon content. In short, the degree of conversion is higher in the younger New Brunswick shales. These shales, of younger geological age probably have a higher carbon to hydrogen ratio than the older Devonian shales. Plotting of the results of the hydrogen retorting on Figure 8 did not reveal as simple a relationship between carbon content and oil yield as obtained for the Fischer tests.

In summary, carbon conversion of more than 70 per cent can be obtained in the higher grade shales of 20 gals/ton and above by the Fischer assay. Liquid yields were not

improved by retorting under hydrogen pressures of 500 psi at 500° and 700°C.

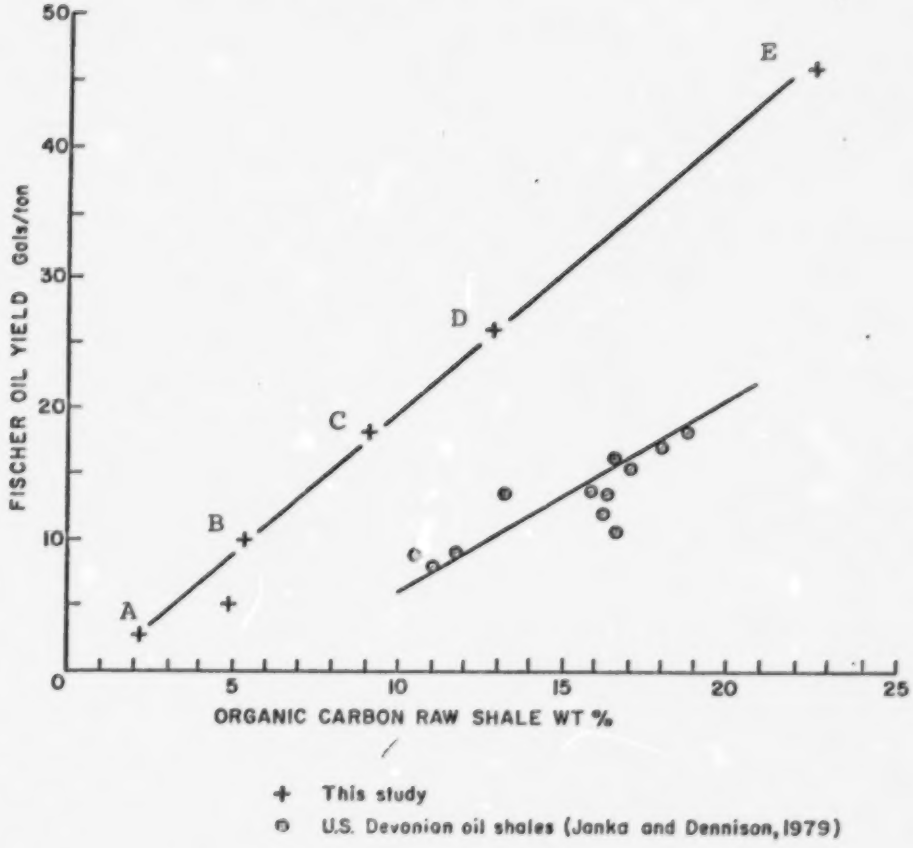
It is important to note, however, that work at the Institute of Gas Technology (IGT) indicated that the Albert shales gave increased oil yields when retorted under hydrogen pressures. A shale with a Fischer assay of 11.1 gals/ton yielded 30.3 gals/ton when retorted under hydrogen (Feld-ldkirchner, H.L. 1965).

Future Work

Additional work is needed on retorting both for process development and for resource assessment. The limited number of retorting tests by the Fischer and by the hydrogen method did little to explain the thermochemical complexities of oil distillation which it is necessary to clarify if processes for the recovery of a liquid distillate and other products are to be developed. It is necessary to know more about the kerogen-bitumen-oil-gas pyrolysis reactions that take place as well about coke formation and oil cracking. The effect of retorting conditions on oil shale quality should be determined and the factors controlling carbonate mineral decomposition, other mineral reactions and that for carbon gasification.

As a preliminary to future work and as a check on past results, it will be worth sending selected samples to the IGT for thermobalance analysis and predictions of retorting behaviour.

Resource evaluation of oil shales, other than those in New Brunswick which are already under investigation, can be undertaken. Fischer-type assays on their own, even as a preliminary test, are not adequate. They should be coupled with determination of carbon conversion during retorting. Complimentary to this work will be the utilization of newer analytical methods to judge oil content and retorting behaviour. Delphi Inc. and Chemical Data Systems Inc. market oil shale assay units for this purpose.



RELATIONSHIP BETWEEN FISCHER ASSAY OIL
OIL YIELD AND ORGANIC CARBON

FIGURE 8

TABLE 8

ORGANIC CARBON CONVERSION DURING RETORTING

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Organic carbon Wt% Raw shale	2.15	4.85	5.20	9.20	12.90	22.90
Fischer Test						
Gas wt%	3.01	1.36	3.08	1.77	3.28	3.79
Gal/ton oil	2.9	5.1	10.1	18.6	26.6	47.5
Organic C. wt% spent shale	0.20	2.40	2.00	2.40	3.20	2.80
% carbon converted	90.7	50.5	61.5	73.9	75.2	87.8
Hydrogen Retorting						
700°C Gas wt%	5.35	6.42	10.55	16.13	18.13	20.50
Gals/ton oil 700°C	4.3	3.0	5.3	11.5	14.9	31.2
Organic C. spent shale	1.00	1.70	0.77	1.14	1.62	3.66
% carbon converted	53.0	64.9	85.2	87.6	87.4	84.0
500°C Gas wt%	5.70	5.60	4.27	7.96	6.07	5.20
Gals/ton oil 500°C	4.2	8.5	7.4	7.8	30.1	45.4
Organic C. wt% spent shale	0.6	0.99	2.15	2.28	2.4	3.65
% carbon converted	72.1	79.6	58.7	75.2	84.4	84.1

imperial gallons/short ton

PROPERTIES OF OIL SHALE

Although the contract did not call for an investigation into the nature and characteristics of the oil shale, some knowledge of its composition was essential for the retorting and mineral concentration work undertaken. Details of the sample locations are given in Appendix 2.

Petrography

The core samples are of a banded, fissile, dark-coloured rock, the oil shales of the Albert Formation which King (1963) described as a varved dolomitic organic limestone containing 30 - 40 per cent dolomite, up to 30 per cent organic matter (kerogen) and the remaining rock constituents being quartz and orthoclase feldspar and small quantities of pyrite (Plate 2). MacAuley (1981) pointed out that the "varves" are not glacial but due to the seasonal precipitation of carbonate in the depositional basin. He describes the oil shales as bedded, laminated kerogenous dolomitic marlstones typical of a lacustrine environment.

Petrographic examination of the samples for this investigation of retorting showed that a similar rock was used. The mineral constituents of the oil shale, in order of abundance, are:

dolomite/calcite	10 - 40 per cent
quartz	10 - 40
feldspar (alkali)	5 - 10
muscovite (sericite)	5 - 10
pyrite	<5
apatite	trace
magnetite	trace

Large, 25 micron clastic grains of carbonate, quartz and feldspar are scattered in a fine grained mass of the mineral constituents. In the more oil-rich shales carbonate forms relatively pure bands several millimeters in thickness. The leaner shales are less well bedded and more argillaceous with carbonate contents falling to 10 per cent. Tiny apatite grains are present and pyrite is scattered through the rock as small subhedral crystals and framboids. Pyrite appears in both carbonate and kerogen-rich parts of the rock. Ocassional grains of magnetite occur. The grain size of opague minerals is generally less than 10 microns. Photomicrographs of the oil shales are given in Plate 3.

The oil fraction or solidified hydrocarbon, kerogen, forms up to 30 or 40 percent by volume of the rock. It occurs interstitially to the mineral grains where it is associated with the fine grained mineral constituents. Kerogen also occurs as blebs and lenses up to 0.5 mm in size which are free of mineral inclusions. These entities are amber in colour and could be albertite. In the more oil-rich shales banding is well developed between carbonate and kerogen-rich layers.

The surface, bulk sample is weathered brown. Compositionally, it is similar to the drill core samples. Weathering has resulted in destruction of some of the pyrite to form iron oxides and the low sulphur content (0.07%) indicates the extent of pyrite oxidation. Being a shale of low oil content banding is not developed and the kerogen is interstitial to the mineral constituents.

Chemical Composition

The 6 samples for this study, with a range in oil values from 2.9 to 47.5 gals/ton oil, were analyzed in order to define the properties of the oil shale (Table 9). All determinations were by ASTM techniques or equivalent accepted methods. The composition of other oil shales are given in Appendix 6.

The ultimate analyses shows the amount of determined mineral and organic carbon, i.e. carbon in calcite and dolomite and carbon associated with the kerogen or organic matter. The content of hydrogen, nitrogen and sulphur were measured and the oxygen content was calculated by difference. The proximate analyses gives further data on the composition of the oil shale with information on moisture content, volatiles, ash and, by difference, fixed carbon. Calorific values and specific gravities were also determined. For purpose of this study volatile losses at 600^{o}C were also obtained. Note that these values are consistently lower than volatile determinations under the proximate analyses. The latter analyses involved heating to 950^{o}C which would ensure higher values than obtained at 600^{o}C. "Volatiles" as determined by the ASTM method should be interpreted with care because at the temperatures used decomposition of the carbonate would have taken place which would cause a weight loss unrelated to the organic matter.

Specific Gravity

Specific gravities were measured on the core samples to establish a quick method of obtaining an approximate value for the oil content of the shale (Figure 9). Similar information for the Colorado oil shale is taken from Smith (1969). The Colorado shales appear to have higher oil contents over the range of specific gravities measured or, alternatively, the Albert shales are lighter.

Volatiles at 600°C

The Fischer assay requires a large sample of 100 grams which was not always available especially during the separation tests. Consequently another method was devised which is suitable for small samples of a gram or two. The determination of volatiles loss over one hour at 600°C gave excellent correlation with oil content (Figure 10). This temperature was chosen because it is below the decomposition of the carbonate in the rock and essentially represents the loss of hydrocarbons, hence oil content.

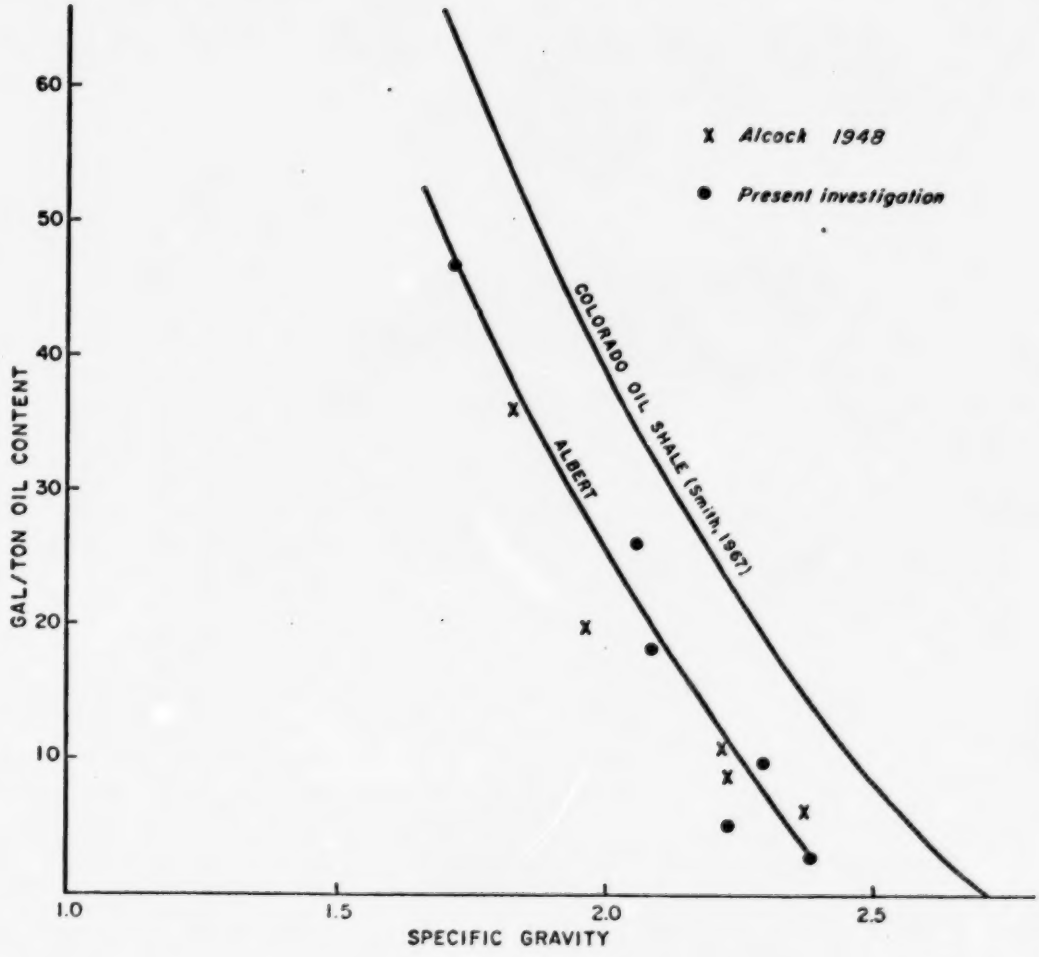
Thermogravimetric analysis

Thermogravimetric analyses of the oil shale series are given in Figure 11 and Table 10. Conclusions on the nature of the oil shale are:

1. The higher the oil content the lower the temperature when weight loss or distillation starts. It was at 330°C for 2.9 gal/ton shale and 100°C for 47.5 gal/ton shale.

2. Distillation or volatilization of the organic fraction proceeds at an even rate to temperatures near 700°C. At this stage decomposition of the carbonate commences as shown by the steepening of the TGA curve.

3. All reactions are essentially complete by 800°C at which stage volatile emmission and calcination is complete. Had heating been under oxidizing conditions, further weight loss would have occurred through combustion of carbon.



SPECIFIC GRAVITY AND OIL CONTENT
FIGURE 9

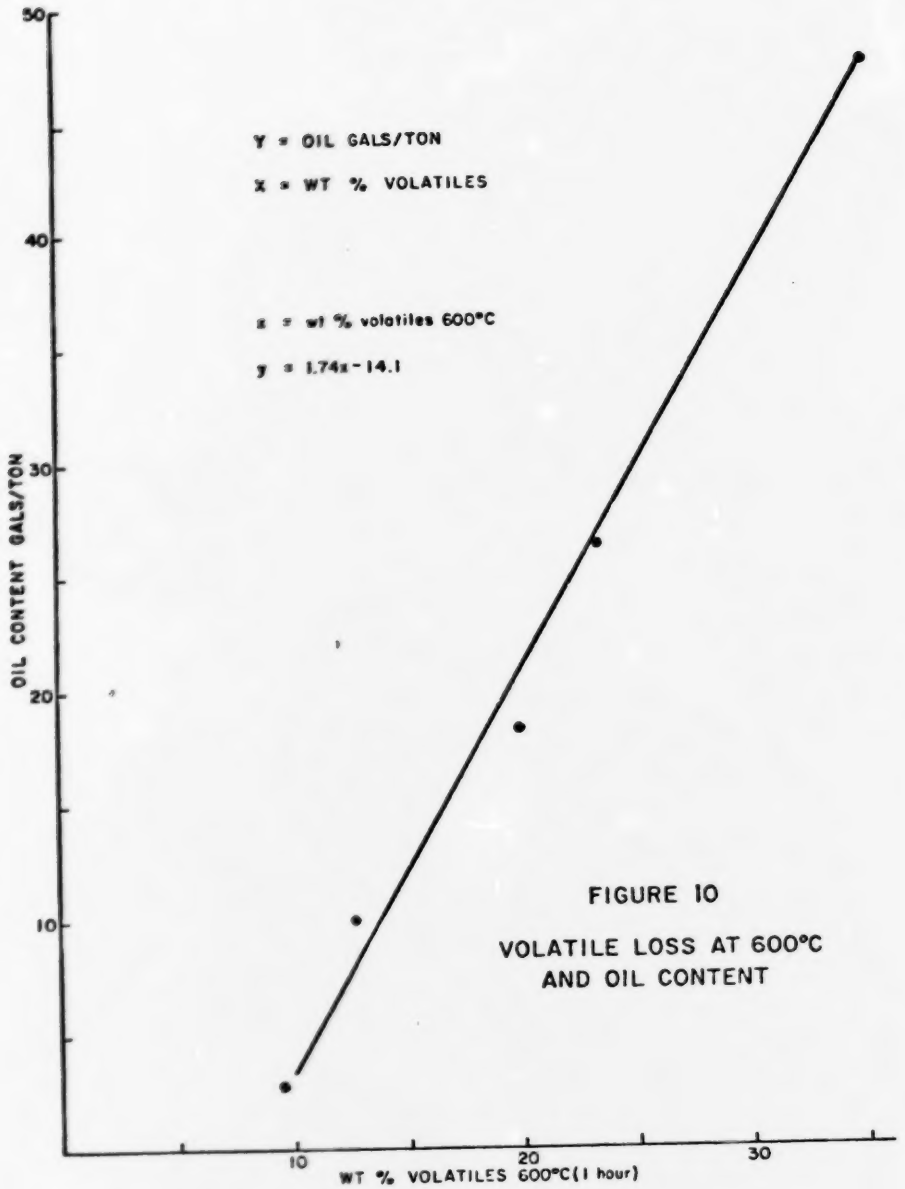
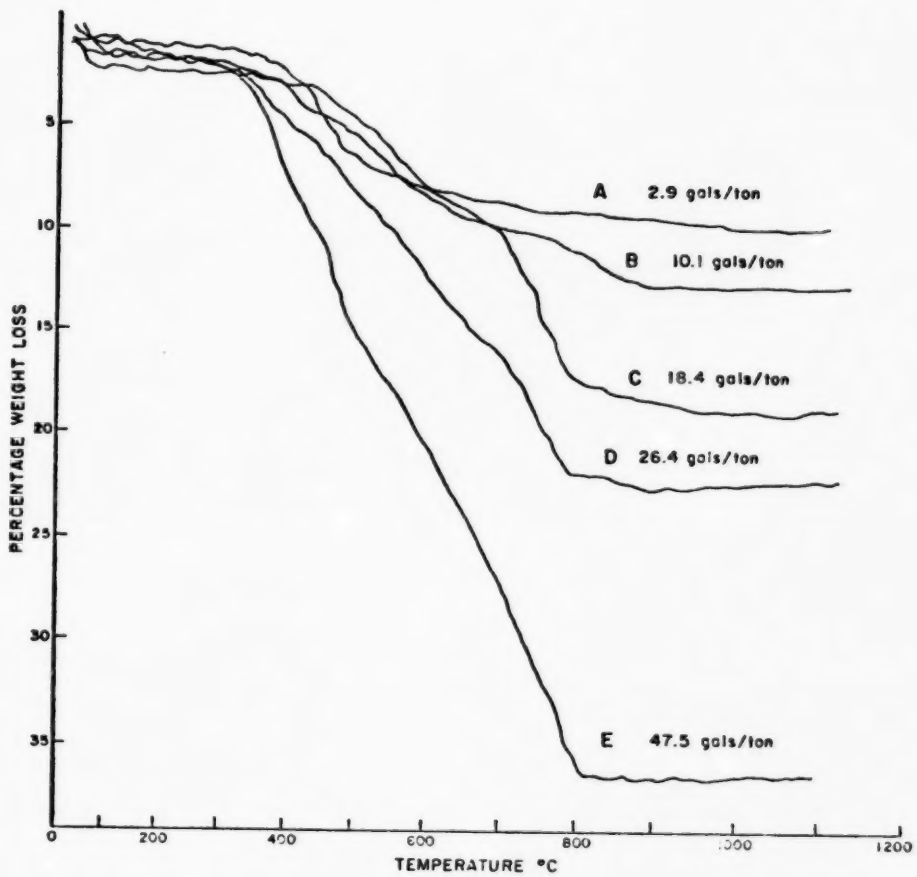


FIGURE 10

VOLATILE LOSS AT 600°C
AND OIL CONTENT



THERMOGRAVIMETRIC ANALYSIS OF OIL SHALES

FIGURE II

TABLE 9

CHARACTERISTICS OF OIL SHALE

	Drill Core A	Surface Outcrop X	Drill Core B	Drill Core C	Drill Core D	Drill Core E
Ultimate Analysis wt% dry						
Mineral Carbon	1.32	1.15	1.82	3.40	4.16	2.76
Organic Carbon	2.15	4.85	5.20	9.20	12.90	22.90
Hydrogen	1.05	1.32	1.55	1.61	2.22	3.09
Oxygen	3.64	3.58	3.97	4.10	6.72	7.16
Nitrogen	0.86	0.93	0.72	0.67	0.82	1.17
Sulphur	0.78	0.07	1.00	0.72	1.18	0.72
Proximate Analysis wt%						
Moisture	1.36	0.83	1.00	0.56	0.42	0.37
Volatile Matter	11.6	16.2	16.0	26.2	35.4	43.6
Fixed Carbon	3.47	6.00	7.02	12.60	17.06	25.66
Ash	90.2	88.1	85.7	80.3	72.0	62.2
Calorific Value						
Btu/lb	431	956	1136	1955	3013	5095
Specific Gravity						
gm/cc	2.39	2.23	2.30	2.09	2.06	1.74
Volatile loss 600°C						
wt%	9.6	13.4	12.8	20.1	23.7	34.5

TABLE 10

RESULTS OF THERMOGRAVIMETRIC ANALYSES

Sample No.	Oil Content Gals/ton	Temperature Wt loss starts	Percentage Wt Loss
A	2.9	330°C	7.6
B	10.1	290	10.8
C	18.4	275	17.6
D	26.4	250	20.6
E	47.5	100	35.4

Experimental condition - nitrogen atmosphere

Heating rate - 10°C per minute

Temperature - to 1100° C

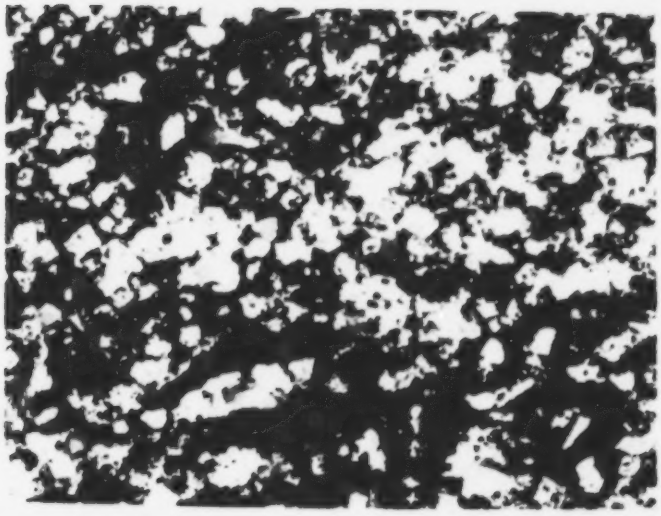
D 26.6 gals/ton

E 47.5 gals/ton

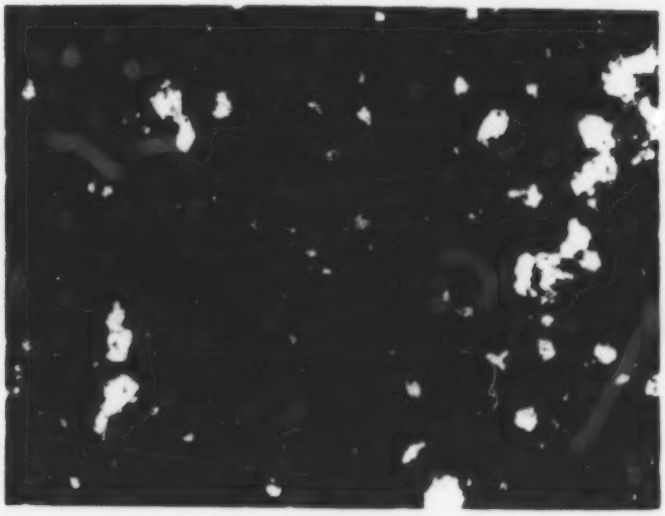
Diamond drill core (diameter ±5cm) showing bedding. Light coloured bands are dolomitic and dark bands are kerogen-rich.

PLATE TWO

PHOTOGRAPHS OF DRILL CORE
DOLOMITIC MARLSTONE



B. 10.1 gals/ton - Low grade dolomitic marlstone with kerogen (dark) interstitial to the dolomite and quartz (light)



E. 47.5 gals/ton - Kerogen-rich dolomitic marlstone. The kerogen (dark) has a wavy, banded structure. Light coloured grains are dolomite and quartz

PLATE THREE
PHOTOMICROGRAPHS OF OIL SHALE
Scale 1 cm. = 80 microns

OIL SHALE UPGRADING

As the improved cost benefit of extracting petroleum from a higher grade shale feed could possibly offset the expense of pretreatment, efforts were made to test the technical feasibility of producing a kerogen enriched fraction from low grade shale containing less than 10 gals/ton oil. In all tests the shale used was from the bulk surface sample which contained 5-7 gals/ton oil. Low grade material was used because it was available in large quantitites and it is such material which would be the subject of an upgrading process. Methods tested for concentration of the kerogen were by size separation, spherical agglomeration, gravity separation and by flotation.

Size Separation

The shale was crushed to -8 mesh and screened in 5 fractions to -325 mesh and each screen size was analyzed for oil content (Table 11). The results show that the oil content of each size fraction remained between 5.3 and 5.0 gals/ton indicating that communition and kerogen liberation over the sizes investigated did not lead to concentration of kerogen over a particular size range. Confirmatory work by Gonzales (1981) at the University of New Brunswick gave similar results.

Gravity separation

The mineral constituents of the shale, quartz, carbonate etc. have specific gravities in excess of 2.7, while kerogen and albertite have a specific gravity near 1. Hence, providing liberation of the kerogen from the mineral grains is reasonably complete gravity separation should provide an effective method of producing a concentrate of the kerogen constituents.

Sink-float tests with bromoform mixture at specific gravities between 2.0 and 2.58 give the results shown in Table 12. The following conclusions can be drawn from these tests.

1. Little separation of kerogen from the mineral grains taken place below SG 2.

2. Concentrates with up to 76 gals/ton oil can be produced between SG 2.0 and 2.5 but yields are less than 2 per cent.

3. Mineralogical examination of the concentrate showed that small quantities of quartz, mica and carbonate were associated with the kerogen grains indicating the difficulty of freeing kerogen from the mineral matter even below -325 mesh.

Spherical agglomeration

Concentration by spherical agglomeration was attempted because this technique works with coal and tar sands which are other types of solidified hydrocarbon (Table 13).

In the first tests pulverized shale -200 mesh was disaggregated in a solution containing 10 ml of 0.2 wt per cent sodium carbonate for 5 minutes. Oil-water emmulsion (2 ml oil/200 m. water) was added and agitation took place in a high speed blender for various periods of time. Number 2 and 6 oil, kerosene and varsol were tried in succession in tests 6, 7, 8, and 9. No kerogen-oil agglomerates formed which could be retained on a screen.

Advice was sought from NRC about appropriate agglomeration technology. As a result, techniques were tried that had been used by R. Farnand (personal communciation) of the Division of Chemistry on other oil shales. Shale was ball milled with dilute acid, hydrochloric in test 1 and sulphuric in tests 2, 3 and 4 to grain sizes of -325. During the process significant quantities (10 to 20 per cent) of the carbonate fraction was dissolved. The ball mill contents were filtered, remixed with 30 per cent water (test 1) and with varsol/sulphuric acid (tests 2 and 3) and rolled again in the ball mill for various lengths of time. Filtering through a 60 mesh sieve produced a kerogen-oil agglomerate which represented a yield of 5 to 48 percent of the starting material. Oil values ranged from 2.6 to 21.8 gals/ton.

A final test involving ball milling with water only and agglomeration with a mixture of heptane/turpentine failed to produce an agglomerate concentrate (test 5).

Flotation

Coal flotation techniques were tried. The double flotation method of the US Bureau of Mines which involves floating the coal using kerosene and methyl isobutyl carbinol did not work. This process depends on lowering the pH below 5 by the addition of hydrochloric acid which was not possible with these oil shales with significant quantities of carbonate.

Conclusions

Best results in preparing a cencentrate or kerogen-rich fraction was obtained by gravity separation of finely ground shale. Work was not extended to find a commercially viable upgrading process using gravity.

Gravity separation can be used to produce an oil enriched fraction. Using -2 inch western shale with 13 gals/ton oil in a heavy media cyclone process 70 per cent of the oil was retained while rejecting 60 per cent of the waste rock. (Mining World 1981). This was equivalent to 80 per cent oil recovery in a fraction containing about 30 gals/ton oil.

The testing of larger samples of Albert shale at a coarse grind in a laboratory is required.

TABLE 11

OIL CONTENT OF SCREENED OIL SHALE

Mesh Size	Sample Grams	Sample Wt%	Oil Content Gals/ton	Cumulative Percentages Wt%	Cumulative Percentages Oil
This Study:					
8 - 30	102.7	53.3	5.3	53.3	5.3
30 - 100	61.1	31.6	6.0	84.9	5.6
100 - 200	13.4	6.9	6.4	91.8	5.6
200 - 325	7.0	3.1	5.8	94.9	5.6
- 325	9.1	4.7	4.8	99.6	5.6
Gouzalez (1981):					
¼ - 8	15.78	8.2	6.4	8.2	6.4
8 - 30	103.96	53.7	5.5	61.9	5.6
30 - 100	46.60	24.1	4.1	86.0	5.2
100 - 250	15.24	7.9	4.3	93.9	5.1
250 - 325	5.47	2.8	4.1	96.7	5.1
- 325	6.38	3.3	3.9	100.0	5.0

TABLE 12

CONCENTRATION OF KEROGEN BY GRAVITY SEPARATION

SG Float	Sample Wt. grams	Yield Wt%	Oil Content Gal/ton
2.58	53.2	88	7.1
2.34	16.20	18	18.4
2.28	9.40	6	30.4
2.00	2.75	2	76.3

Shale ground to -325 mesh

Oil content of starting material 7.0 gals/ton

TABLE 13

KEROGEN CONCENTRATION BY AGGLOMERATION
-200 mesh shale

Test	Conditioning Agent	Acid Treatment	Agglomeration Additives	Results Conc. Yield (wt%)	Oil (gals/ton)
1	toluene toluene	HCl	-	15 40	4.5 4.4
2		H_2SO_4	Varsol/H_2SO_4	41 6	2.8 2.6
3		H_2SO_4	Varsol/H_2SO_4	5 48	21.8 3.2
4			Heptane/Turpentine	no agglomeration	
5			Toluene	no agglomeration	
6	dispersent		No. 2 oil	no agglomeration	
7	dispersent		No. 6 oil	no agglomeration	
8	dispersent		Kerosene	no agglomeration	
9	dispersent		Varsol	no agglomeration	

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REQUIREMENT I:

1. Design an apparatus for hydroretorting that meets the approval of the Scientific Authority or his designated representative. This apparatus will be of a size able to accommodate 50-60g of samples and can be operated up to pressures of 500 psi and at temperatures up to 700°C. This will require visits of key personnel to CANMET's Energy Research Laboratories as well as to the Institute of Gas Technology in Chicago.

2. Construct the apparatus as well as procure the required components.

3. Set up an apparatus for making conventional Fischer assays that meets the approval of the Scientific Authority.

4. Acquire six (6) samples of oil shale that cover an appropriate range of kerogen contents.

5. Establish the required experimental techniques and expertise for both hydroretorting and Fischer assays.

6. Obtain reliable data on the six (6) samples at appropriate ranges of temperatures, pressures, rates of heating, particle size that are approved by the Scientific Authority. The sought data includes both liquid and gaseous yields, elemental analyses, ash content, calorific value, pour and cloud points as well as gas chromatographic simulated distillation data.

REQUIREMENT II:

The second part of the program will involve attempts to make a kerogen-rich concentrate for subsequent oil extraction. Communition of oil shale will be followed by concentration through standard methods of physical separation viz. gravity, screening, agglomeration and flotation. Microscopy and analyses will be required in support of this beneficiation study.

REPORTS:

Monthly progress reports will be required and shall accompany monthly progress claims.

A final report in five (5) copies and ten (10) microfiche copies (in card format 24X reduction, 4" x 6" sheets of silver halide film) of the report are to be submitted. This report must be comprehensive on all facets of the work and must include sufficient drawings, sketches, photographs, and discussion of problems and successes associated with the work to facilitate a full and accurate evlauation of the work by the Scientific Authority. This report will be prepared in accordance with good engineering practices and will include, as a minimum, the following: list of contents, summary or abstract, introduction, technical discussion, conclusions and supporting graphs, tables and figures as applicable.

Each report is to contain a cover page (sample attached).

APPENDIX 2

SAMPLES

The samples of oil shale required for the project were acquired by courtesy of the Mineral Resources Branch of the New Brunswick Department of Natural Resources. Five, of various oil content, were fresh rock from diamond drill hole number 2 (45° 52'47", 64° 41'51") of Canadian Occidental Petroleum Ltd. located near the village of Albert Mines:

A	0 - 10 gals/ton *	685' - 688'
B	10 - 19	688' - 689', 695' - 698' 728' - 730'
C	20 - 29	475' - 476', 506' - 507' 689' - 690'
D	30 - 39	499' - 500', 514' - 516' 580' - 581', 582' - 583'
E	40 - 59	530' - 531', 541' - 543' 549' - 550'

The sixth, a bulk sample, was from a surface exposure near the diamond drill hole about ½ mile from Albert Mines. It contained 5 - 7 gals/ton oil.

* Imperial gals/short ton

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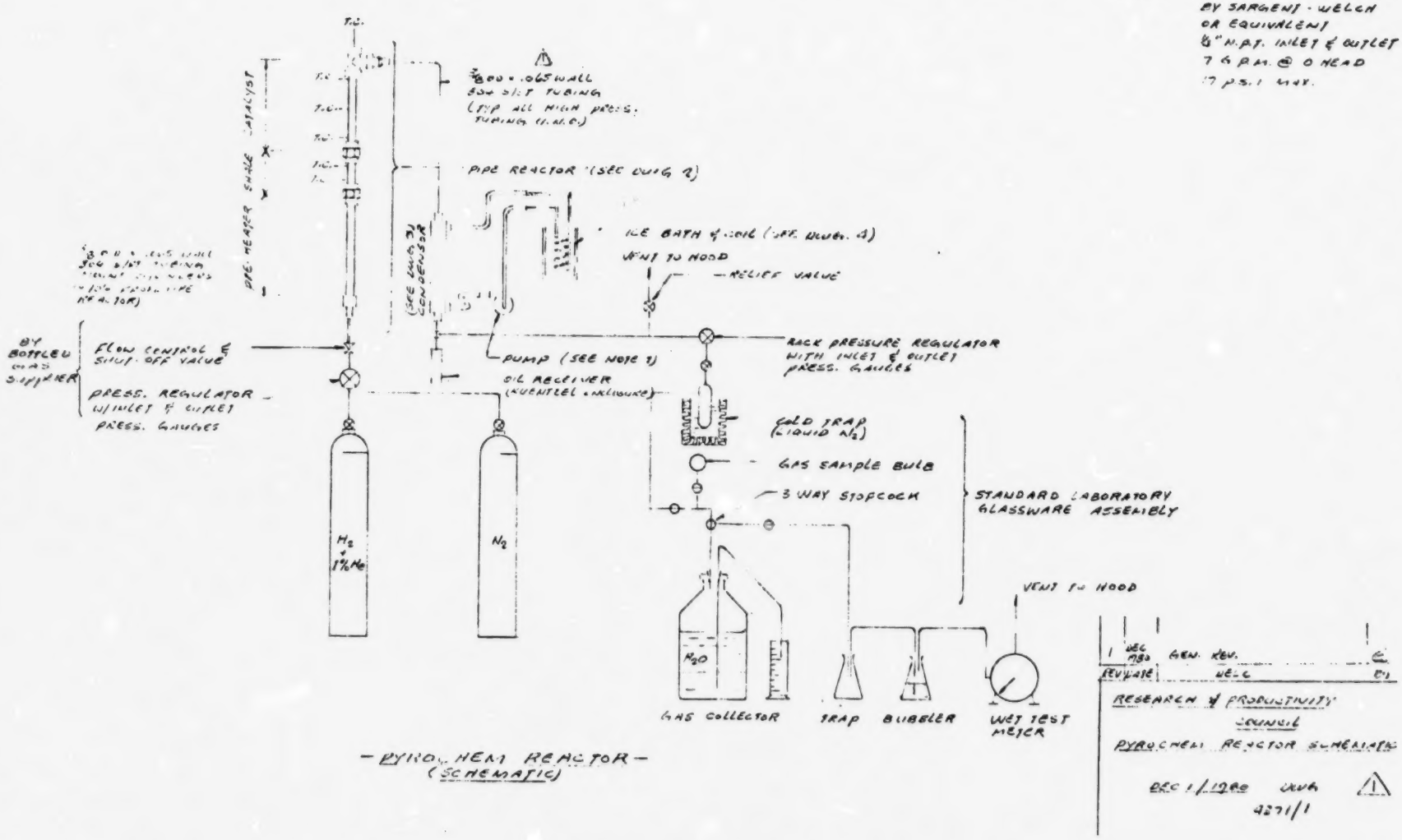
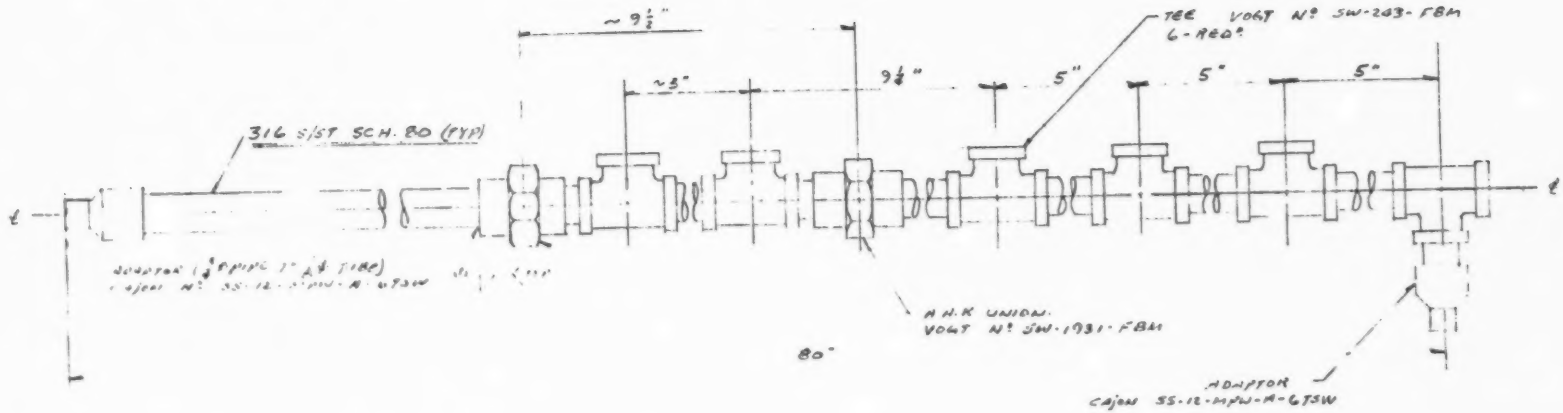

NOTES
1. PUMP - # 7158B AS SUPPLIED BY SARGENT - WELCH OR EQUIVALENT 1/4" N.P.T. INLET & OUTLET 7 G.P.M. @ 0 HEAD 17 P.S.I. MAX.
PRE-HEATER SHALE CATALYST
T.C.
3/8 OD x .065 WALL 304 S/S T. TUBING (TYP ALL HIGH PRESS. TUBING (U.N.O.)
PIPE REACTOR (SEE DWG 2)
(SEE DWG 3) CONDENSER
ICE BATH & COIL (SEE DWG. 4)
VENT TO HOOD
RELIEF VALVE
BACK PRESSURE REGULATOR WITH INLET & OUTLET PRESS. GAUGES
PUMP (SEE NOTE 1)
OIL RECEIVER (ERLENMEYER FLASK)
BY BOTTLED GAS SUPPLIER
FLOW CONTROL & SHUT-OFF VALVE
PRESS. REGULATOR W/INLET & OUTLET PRESS. GAUGES
COLD TRAP (LIQUID N2)
GAS SAMPLE BULB
3 WAY STOPCOCK
STANDARD LABORATORY GLASSWARE ASSEMBLY
H2 + 1% He
N2
H2O
GAS COLLECTOR
TRAP
BUBBLER
WET TEST METER
VENT TO HOOD
GEN. REV.
REVISIONS
RESEARCH & PRODUCTIVITY COUNCIL
PYROCHEM REACTOR SCHEMATIC
DEC 1/1980 DWN
4271/1

- PYROCHEM REACTOR - (SCHEMATIC)

APPENDIX 3A
MODIFIED PYROCHEM APPARATUS



– PIPE REACTOR –
(N.T.S.)

NOTES

1). DESIGN PRESS 1000 PSIG
TEMP. 1000 °F

2) OPERATING PRESS 500 PSIG
TEMP 1000 °F

3) FITTINGS MAY BE SUBSTITUTED BUT MUST BE 316 S/ST MATL AND RATED 3000 PSI C.W.P.

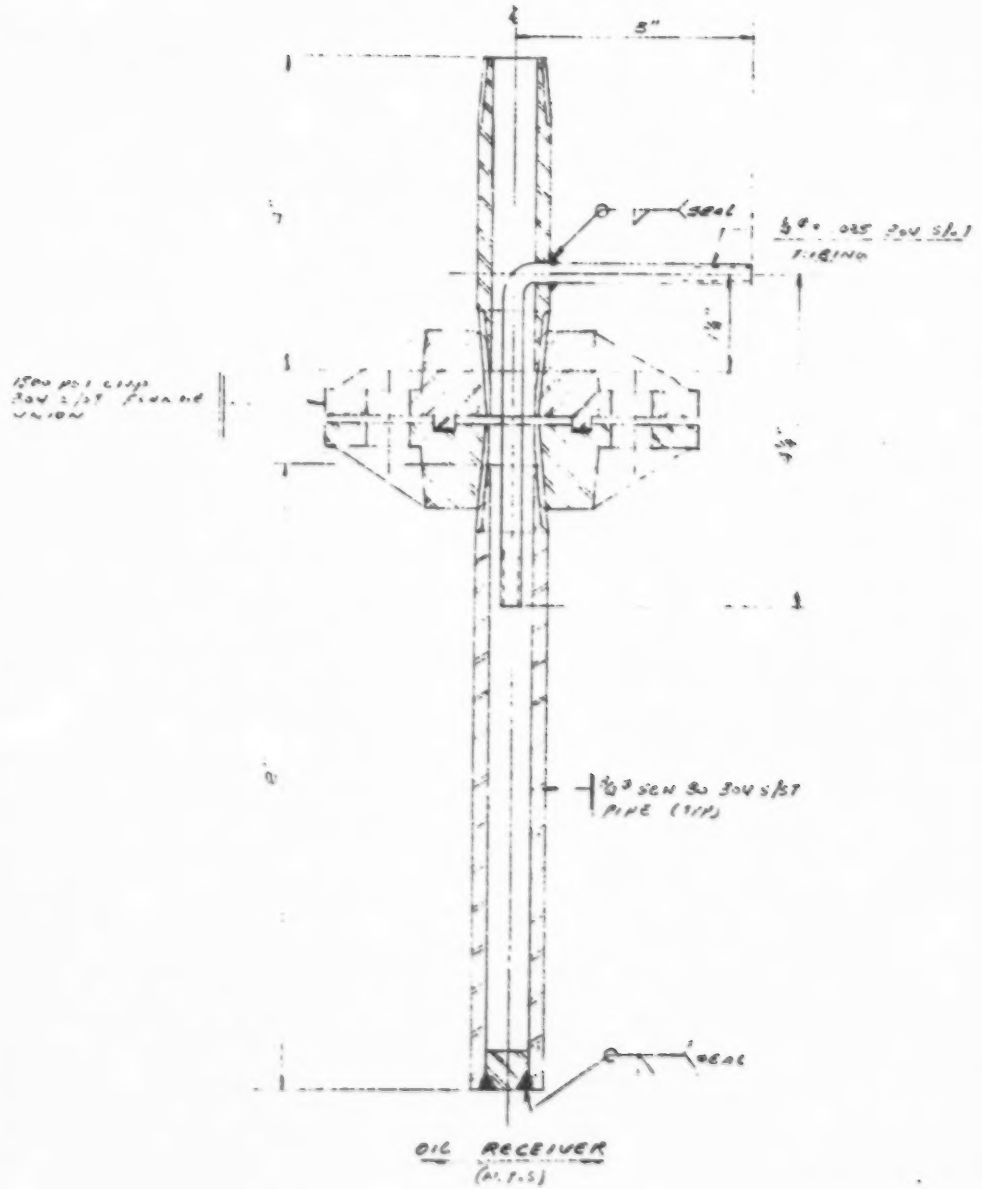
1	DEC 1980	GEN REV	GY
No.	DATE	DESC.	BY

RESEARCH & PRODUCTIVITY COUNCIL

PYROCHEM REACTOR
PIPE REACTOR DETAILS

DEC. 1/1980 DWG. 4371/3 1

APPENDIX 3B
PIPE REACTOR



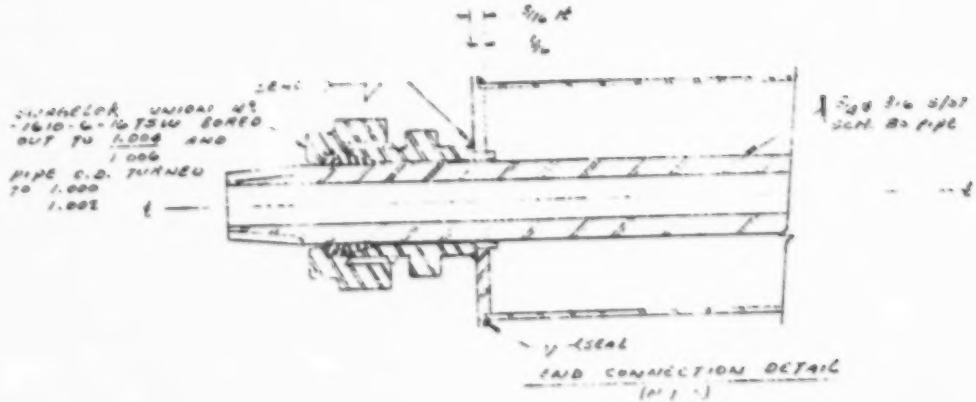
APPENDIX 3C
KEUNTZEL PRESSURE VESSEL

RESEARCH & PRODUCTIVITY COUNCIL

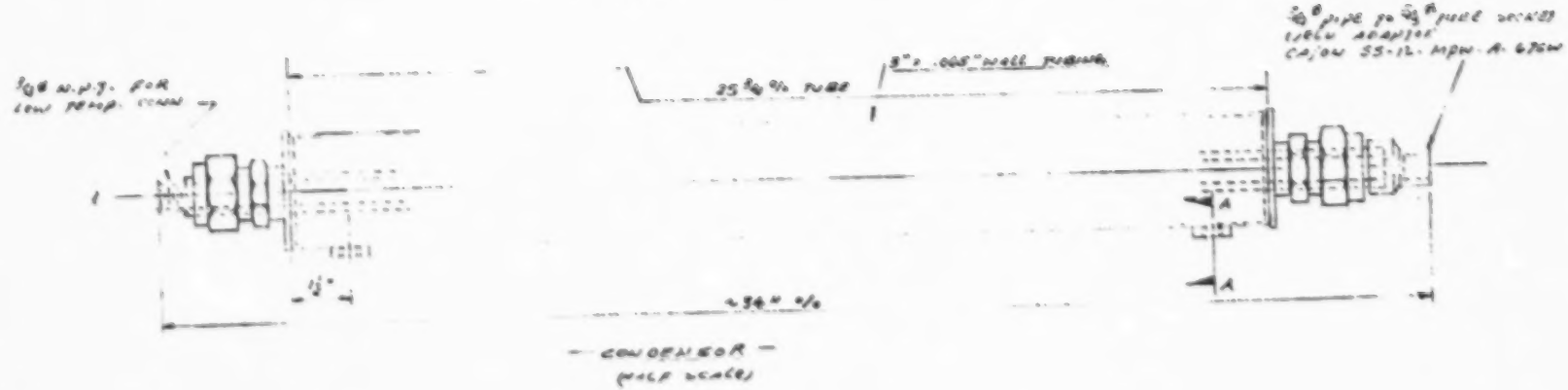
PYROCHEMICAL REACTOR

OIL RECEIVER DETAILS.

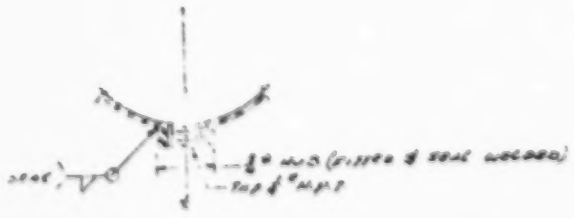
DEC 2/1980 DWG 5 ⚠



END CONNECTION DETAIL
(FULL SCALE)



CONDENSOR
(HALF SCALE)

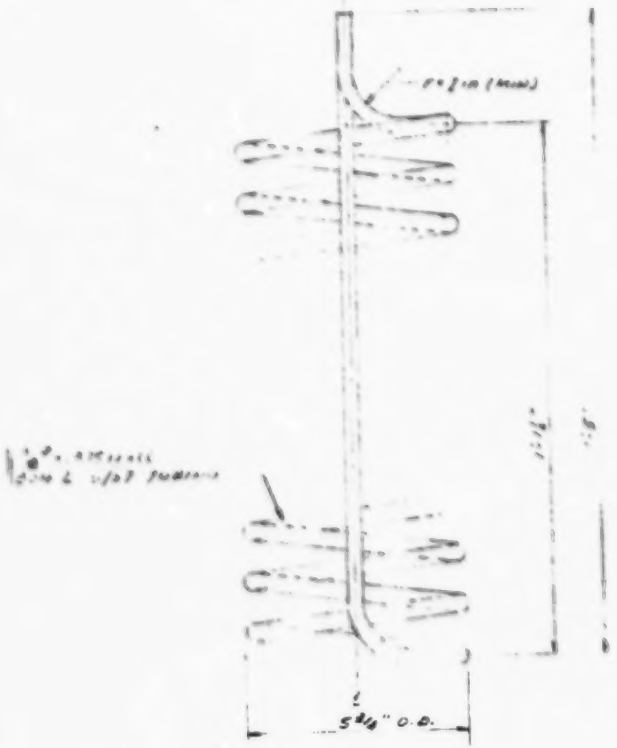


SECTION A-A
(FULL SCALE)

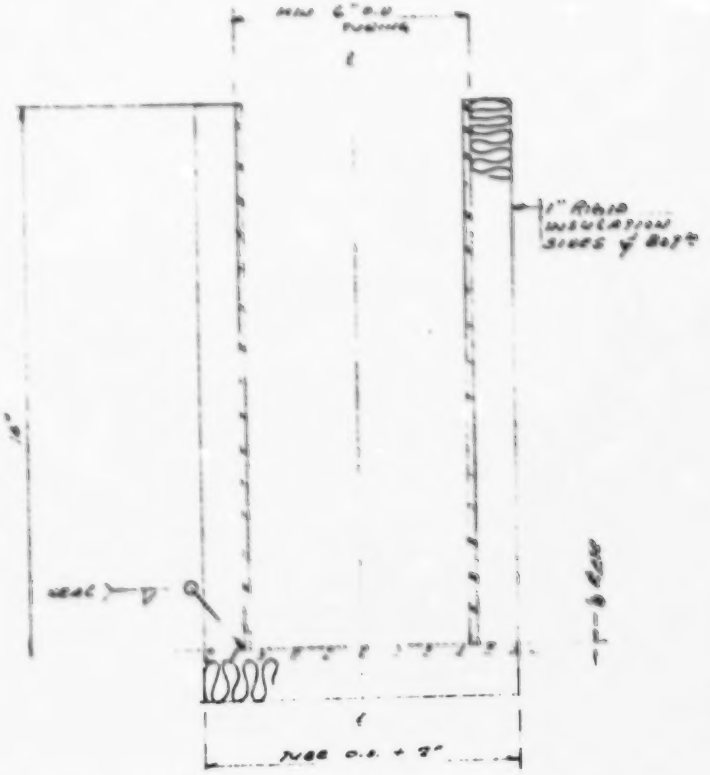
RESEARCH & PRODUCTIVITY COUNCIL

NUCLEAR REACTOR
CONDENSOR DETAILS

APPENDIX 3D
CONDENSER DETAILS



COOLING COIL
(HALF SCALE)



BATH CONTAINER
(SECTION HALF SCALE)

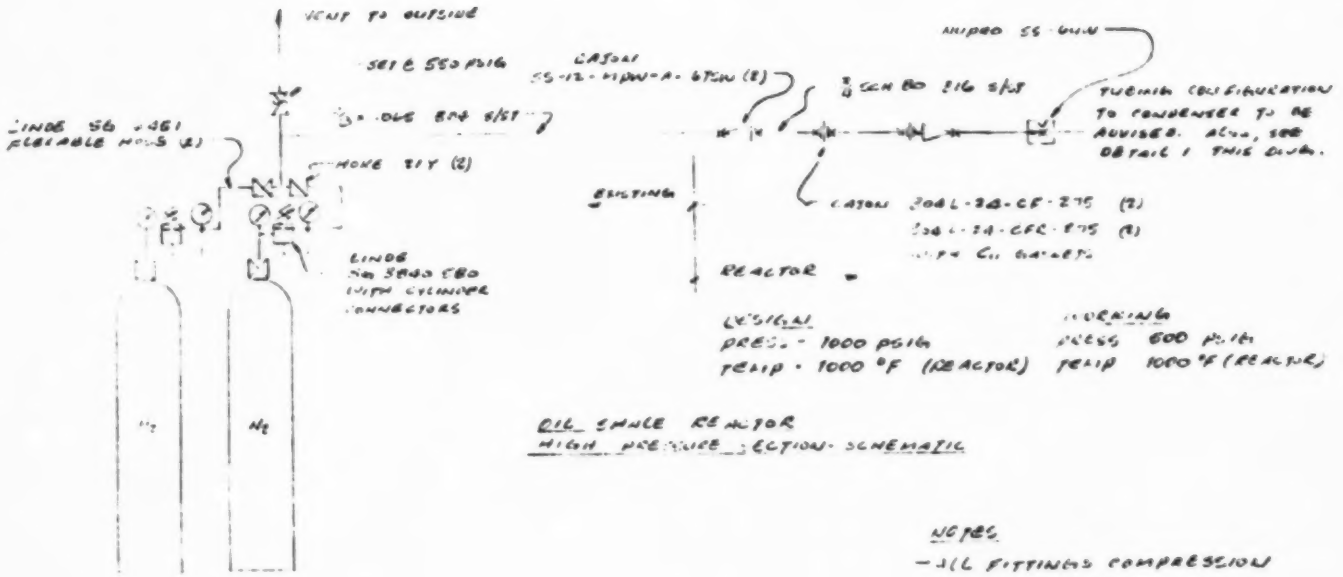
APPENDIX 3E
ICE BATH AND COIL

RESEARCH & PRODUCTIVITY COUNCIL

PYROCHEM REACTOR

ICE BATH & COIL

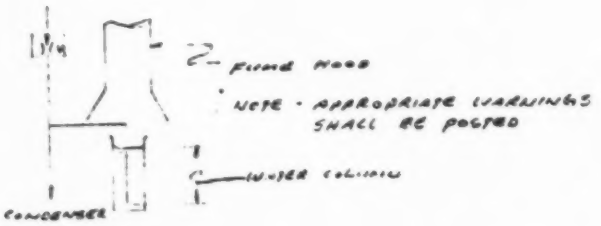
DEC 1/1980 DWG. M871/41 10



OIL SHALE REACTOR
HIGH PRESSURE SECTION - SCHEMATIC

NOTES

- ALL FITTINGS COMPRESSION TYPE (SWAGELOK) UNLESS SHOWN AS WELDED.
- REACTOR TO BE MOUNTED VERTICALLY AND APPROVED BY INDUSTRIAL TECHNOLOGY (3)



DETAIL 1

FLOW CONTROL AND LOW PRESSURE SAFETY DEVICE - BY INDUSTRIAL TECHNOLOGY (3)

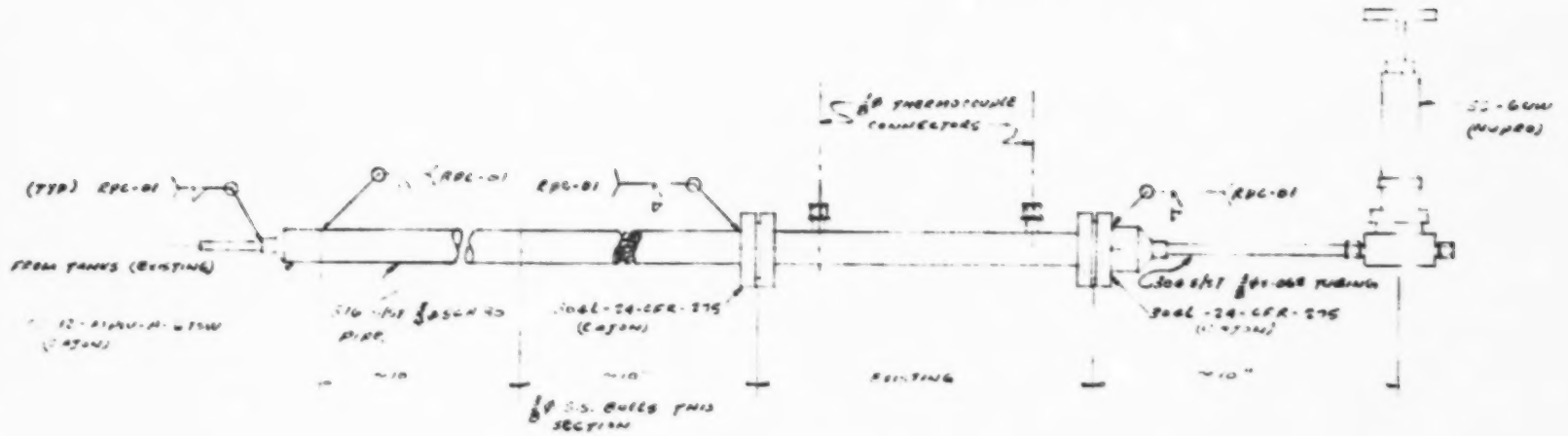
RESEARCH & PRODUCTIVITY COUNCIL

OIL SHALE REACTOR (REVISED)

SCHEMATIC

By BL JULY 28/81 037i-1R

APPENDIX 4A
REDESIGNED PYROCHEM APPARATUS



NOTES

1. REACTOR TO BE MOUNTED VERTICALLY
2. "SNOOP" TEST ASSEMBLY AT 500 PSIG
3. PRESSURE TEST ASSEMBLY AT 750 PSIG

RESEARCH & DEVELOPMENT COUNCIL

BIG SMALL REACTOR (REVISED)

DETAILS

By G. AUG. 25/81

J371-2 R

APPENDIX 4B
REDESIGNED PIPE REACTOR

APPENDIX 5

TEMPERATURE PROGRAMMED GAS CHROMATOGRAPHY LABORATORY REPORT

Three distillate oils were submitted for "Temperature-programmed gas chromatography". Known weights of each were diluted to 25 mL with hexane "Spectrograde" and further diluted 5 mL to 50 mL to yield solutions containing ~1 mg oil/mL solvent.

Analyses were performed using a Hewlett-Packard 5830A gas chromatograph equipped with a 2 m x 4 mm 3% OV-1 on Gas Chrom Q (100/120 mesh) column and flame ionisation detectors (FID). The following parameters were used for the temperature programme:

Inject sample (2 µL)
Hold column temperature @ 35°C for 5 minutes.
Programme @ 8C/min, from 35°C to 300°C
and hold @ 300°C for 20 minutes.
Carrier gas flow: N_2 @ 30 mL/min.
F.I.D.: H_2 @ 30 mL/min.
Air @ 300 mL/min.
Injector Temperature = 220°C
Detector Temperature = 375°C
Attenuation: 2' (all samples)

Chemistry Lab Code	Label	Final Concentration
81/861	X - Composite Fischer Assay Oil	1.03 mg/mL
81/862	Y - Hydrogen retorting @ 500°C oil	1.07 mg/mL
81/864	W - Composite of hydrogen retorting add. @ 700°C.	1.101 mg/mL

DISCUSSION

A maximum column temperature of 300°C was selected based on the results of a preliminary programme to 350°C, in which severe tailing was experienced.

The attenuation of 2' was selected as a compromise between high definition for the lower boiling point components and off-scale peaks for the higher boiling point components, compared to, poor definition of the lower boiling point components and on-scale peaks for the higher boiling point components.

We note that the oils possessed different solubilities in hexane. The initial dilutions of "W" and "X" yielded dense dark brown suspensions in orange-brown solutions. The suspensions rapidly settled out as dark brown flocs. The initial dilution of "Y" yielded a light, pale orange-brown suspension in a light orange-brown solution, which settled out as a floc.

In all three cases the final 1:10 dilution of each suspension yielded solutions essentially free of suspended solids.

APPENDIX 6

ANALYSIS OF US AND CANADIAN OIL SHALES
FELDLSIRCHNER 1965

State or Province Formation County Laboratory No.	Colorado Green River Garfield 4388	New Brunswick Albert Albert 4782	Indiana New Albany Jackson 4588	Kentucky New Albany Marion 4498	Tennessee Chattanooga Cheatham 4586	Illinois Coal Measure Fulton 4474
Ultimate Analysis, wt%(dry)						
Mineral Carbon	4.96	3.05	2.57	3.10	0.21	1.55
Organic Carbon	17.29	15.14	6.74	11.17	11.22	16.13
Hydrogen	2.42	2.27	0.99	1.38	1.30	1.60
Sulphur	0.71	0.70	1.64	2.30	6.66	2.56
Fischer Assay						
Oil, wt%	13.7	11.1	3.1	5.2	3.7	4.0
Water, wt%	1.1	1.7	0.8	0.9	0.7	4.2
Gas + Loss, wt%	3.0	2.8	1.3	1.9	2.4	1.8
Oil, gal/ton dry shale	35.9	30.3	7.8	I3.3	9.5	10.4
Specific Gravity of oil, 60°F/60°F	0.914	0.876	0.956	0.944	0.934	0.948

APPENDIX 7

MAJOR AND MINOR ELEMENTS (wt%)

	Shale
SiO_2	42.34 - 65.42
TiO_2	0.72 - 1.28
Al_2O_3	0.20 - 19.80
Fe_2O_3	5.27 - 8.89
MnO	0.0 - 0.23
MgO	1.62 - 6.88
CaO	1.79 - 19.77
Na_2O	0.67 - 4.90
K_2O	0.04 - 4.39
P_2O_5	0.39 - 2.58
S	0.05 - 0.56

Average of 14 analyses taken from Abbott & Barnett, 1968.

APPENDIX 8

TRACE ELEMENTS (ppm)

	Shale[1]	Average[2]	Range[2]
Antimony	<200	-	-
Arsenic	<500	-	-
Barium	500 - 1000	102	40 - 220
Beryllium	-	6	2 - 13
Bismuth	<10	-	-
Boron	<50	0.54	0.098 - 1.63
Cadmium	<50	-	-
Cerium	-	-	-
Chromium	50 - 200	72	16 - 128
Cobalt	<50	-	-
Copper	50 - 200	66	10 - 200
Fluoride	-	538	230 - 2200
Gallium	10	N.D.	N.D.
Germanium	10	-	-
Gold	-	0.185	0.10 - 0.40
Lead	50 - 200	49	16 - 122
Lithium	-	62	9 - 165
Molybdenum	<50	22	9 - 83
Nickel	30 - 50	47	13 - 66
Phosphorous	-	900	90 - 16600
Rubidium	-	54	10 - 114
Silver	500 - 2000	3	2 - 7
Strontium	500 - 2000	664	49 - 2060
Tantalum	1000	-	-
Thorium	-	-	-
Uranium	-	7	2 - 17
Vanadium	200	88	11 - 260
Zinc	-	73	9 - 140
Zirconium	100 - 200	-	-

[1]Abbott, D., Barnett, D. E. 1968 (average 14 analyses). Ashed Shales

[2]Pickerill, P. K. and Carter, D. 1980 (average 47 analyses) Raw Shale